Theoretical Chemistry

Frédéric Castet

frederic.castet@u-bordeaux.fr
Summary

• The Hartree-Fock-Roothaan method
• Pople and Dunning basis sets
• Semiempirical models
• Configuration interaction
• Möller-Plesset perturbation theory
• Density functional theory
• Time-dependent DFT
**HARTREE-FOCK METHOD**

**Single determinant wavefunction**

\[
\Phi_{\text{HF}} = \frac{1}{\sqrt{(2N)!}} \left[ \begin{array}{cccc}
\psi_1(r_1) & \psi_2(r_1) & \ldots & \psi_{2N}(r_1) \\
\psi_1(r_2) & \psi_2(r_2) & \ldots & \psi_{2N}(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(r_{2N}) & \psi_2(r_{2N}) & \ldots & \psi_{2N}(r_{2N})
\end{array} \right]
\]

**Spin-orbitals**

\[
\psi_{\mu}(r_{\mu}) = \phi_{\mu}(r_{\mu}) \times \xi_{\mu}(\sigma_{\mu})
\]

Spin function \( \alpha \) or \( \beta \)
Atomic or molecular orbital

**Linear Combination of Atomic Orbitals (Roothan)**

\[
\phi_i(r) = \sum_{p=1}^{M} C_{pi} \chi_p(r)
\]

Atomic functions
Expansion coefficients = *variational parameters*
**HARTREE-FOCK METHOD**

*H₂ molecule in the LCAO approximation*

\[ \Phi_{HF}(1,2) = \frac{1}{\sqrt{2}} \sigma_g(1)\sigma_g(2) \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \]

\[ \sigma_g = \frac{1}{\sqrt{2(1 + S)}}(1s_A + 1s_B) \]

\[ \sigma_u = \frac{1}{\sqrt{2(1 - S)}}(1s_A - 1s_B) \]

\[ \Phi_{HF}(1,2) = \frac{1}{4(1 + S)} (1s_A(1) + 1s_B(1))(1s_A(2) + 1s_B(2)) \times [\text{spin}] \]

\[ = \frac{1}{4(1 + S)} \left\{ \begin{array}{c}
1s_A(1)ls_A(2) + 1s_B(1)ls_B(2) + 1s_A(1)ls_B(2) + 1s_B(1)ls_A(2)
\end{array} \right\} \times [\text{spin}] \]

\[ \text{ionic configurations} \]

\[ \text{covalent configurations} \]
HARTREE-FOCK METHOD

$H_2$ molecule in the LCAO approximation

Correlation energy

$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$
Configuration Interaction

CI multi-determinant wavefunction

Linear combination of the reference (HF) configuration and of excited configurations

\[ \Psi = a_0 \Phi_{HF} + \sum_{i=1} a_i \Phi_i \]

\( a_k = \text{variational parameters} \)

**Full CI** = includes all possible excited configurations

Provides the exact (non-relativistic) energy of the ground and excited states (within the chosen LCAO model)
**Configuration Interaction**

CI multi-determinant wavefunction

*Electron configurations for the H₂ molecule in the LCAO approximation*

\[ \Psi_{IC}^{\text{HF}} = a_1 \Phi_1 + a_2 \Phi_2 + a_3 \Phi_3 + a_4 \Phi_4 \]

Combining 4 Slater determinants

→ 4 CI electronic states (ground state + 3 excited states)
CI coefficients obtained from the diagonalisation of the Hamiltonian matrix in the Slater determinants basis

M Slater determinants $\Rightarrow$ CI matrix $H$ of dimension $(M \times M)$

$$H = \begin{pmatrix}
\langle \Phi_1 | \hat{H} | \Phi_1 \rangle & \langle \Phi_2 | \hat{H} | \Phi_1 \rangle & \ldots & \langle \Phi_M | \hat{H} | \Phi_1 \rangle \\
\langle \Phi_1 | \hat{H} | \Phi_2 \rangle & \ldots & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots \\
\langle \Phi_1 | \hat{H} | \Phi_M \rangle & \ldots & \ldots & \langle \Phi_M | \hat{H} | \Phi_M \rangle 
\end{pmatrix}$$

Diagonal terms = energies of each electron configuration
Off-diagonal terms = couplings between the various configurations
CONFIGURATION INTERACTION

Slater rules

*Only 3 types of non zero terms in the CI matrix*

1) $\Phi_i$ and $\Phi_j$ are identical (diagonal terms)

$$\langle \Phi | \hat{H} | \Phi \rangle = \sum_m \langle m | \hat{h} | m \rangle + \frac{1}{2} \sum_m \sum_n [(mm|nn) - (mn|mn)]$$

2) $\Phi_i$ and $\Phi_j$ differ by 1 spin-MO: $\Phi_i = |...m...> ; \Phi_j = |...p...>$

$$\langle \Phi_i | \hat{H} | \Phi_j \rangle = \langle m | \hat{h} | p \rangle + \sum_n [(mp|nn) - (mn|pp)]$$

Brillouin’s theorem: no coupling between the HF and the single excited configurations

$$\langle \Phi_{HF} | \hat{H} | \Phi_{SINGLE} \rangle = \langle m | \hat{F} | p \rangle = 0$$

3) $\Phi_i$ and $\Phi_j$ differ by 2 spin-MOs: $\Phi_i = |...mn...> ; \Phi_j = |...pq...>$

$$\langle \Phi_i | \hat{H} | \Phi_j \rangle = (mp|nq) - (mq|np)$$
**CONFIGURATION INTERACTION**

*General form of the CI matrix*

\[
H = \begin{pmatrix}
\langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle & 0 & \langle \Phi_{D} | \hat{H} | \Phi_{HF} \rangle & 0 & 0 & 0 \\
0 & \langle \Phi_{S} | \hat{H} | \Phi_{S} \rangle & \langle \Phi_{D} | \hat{H} | \Phi_{S} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{S} \rangle & 0 & 0 \\
\langle \Phi_{HF} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{S} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{D} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{D} \rangle & \langle \Phi_{Q} | \hat{H} | \Phi_{D} \rangle & 0 \\
0 & \langle \Phi_{S} | \hat{H} | \Phi_{T} \rangle & \langle \Phi_{D} | \hat{H} | \Phi_{T} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{T} \rangle & \langle \Phi_{Q} | \hat{H} | \Phi_{T} \rangle & \ldots \\
0 & 0 & \langle \Phi_{D} | \hat{H} | \Phi_{Q} \rangle & \langle \Phi_{T} | \hat{H} | \Phi_{Q} \rangle & \langle \Phi_{Q} | \hat{H} | \Phi_{Q} \rangle & \ldots \\
0 & 0 & 0 & \ldots & \ldots & \ldots \\
\end{pmatrix}
\]
**CONFIGURATION INTERACTION**

*Cl matrix for the \( H_2 \) molecule*

4 Slater determinants → CI matrix of dimension (4×4)

\[
H = \begin{pmatrix}
\langle \Phi_1 | \hat{H} | \Phi_1 \rangle & 0 & 0 & \langle \Phi_4 | \hat{H} | \Phi_1 \rangle \\
0 & \langle \Phi_2 | \hat{H} | \Phi_2 \rangle & \langle \Phi_3 | \hat{H} | \Phi_2 \rangle & \langle \Phi_4 | \hat{H} | \Phi_2 \rangle \\
0 & \langle \Phi_2 | \hat{H} | \Phi_3 \rangle & \langle \Phi_3 | \hat{H} | \Phi_3 \rangle & \langle \Phi_4 | \hat{H} | \Phi_3 \rangle \\
\langle \Phi_1 | \hat{H} | \Phi_4 \rangle & \langle \Phi_2 | \hat{H} | \Phi_4 \rangle & \langle \Phi_3 | \hat{H} | \Phi_4 \rangle & \langle \Phi_4 | \hat{H} | \Phi_4 \rangle
\end{pmatrix}
\]

*CI/AM1 calculation*

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</table>
**CONFIGURATION INTERACTION**

\[ \Phi_{\text{HF}}(1,2) = \frac{1}{\sqrt{2}} \sigma_\varphi(1) \sigma_\varphi(2) \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \]

50\%(\text{H}^+/\text{H}) + 50\%(\text{H}·/\text{H})

\[ \Psi = a_0 \Phi_{\text{HF}} + \sqrt{1 - a_0^2} \Phi_{\text{D}} \]

\[ a_0 = f(R) \]
CONFIGURATION INTERACTION

\[ R \to R_{eq} \Rightarrow a_0 \to \approx 1 \]

\[ \Psi \approx \Phi_{HF} \]

\[ R \to \infty \Rightarrow a_0 \to \frac{1}{\sqrt{2}} \]

\[ \Psi = \frac{1}{\sqrt{2}} \Phi_{HF} + \frac{1}{\sqrt{2}} \Phi_D \]
Practical limitation of CI: Large systems

Cl expansion over M Slater determinants

\[ \Psi^{\mu IC} = \sum_{k=1}^{M} C_k \Phi_k \]

N electrons in K MOs
Number of Slater determinants: combinatorial explosion

\[ M = C_N^{2K} = \frac{2K!}{N!(2K - N)!} \]

Example of benzene (valence electrons, single-zeta minimal basis set):  
N = 30 electrons in K = 30 valence MOs \( \rightarrow M = 1.18 \times 10^{17} \)

*Full CI impossible in most cases*
CONFIGURATION INTERACTION

Truncated CI calculation

Selection of a small number of "active" MOs

- Always unoccupied
- Active MO space
- Always occupied

Selection of a few types of electron excitations

- Only Singles (SCI)
- Singles + Doubles (SDCI)

If all possible types of excitation within the active space are included:
→ Complete Active Space (CAS) calculation

Note:
SCI does not change the total energy of the ground state compared to HF (Brillouin’s theorem). Frequently used for simulating absorption spectra.
Active space definition

The active space should:
- be « sufficiently large » (tests vs. size)
- respect the symmetry of the molecule (MOs degeneracies)
- (for photo-chemistry) include all the MOs of interest along all the reaction path

Example of benzene

CI(15,16) = (HOMO,LUMO) not correct
CI(13,17): not correct
CI(12,17) or CI(14,17) are correct
**MULTI-CONFIGURATIONAL SCF**

Refinements of the CI scheme

\[ \Psi = a_0 \Phi_{HF} + \sum_{i=1}^{n} a_i \Phi_i \]

**MC-SCF:** LCAO coefficients re-optimized in each excited configuration

**CAS-SCF:** Complete Active Space SCF
Account for *all possible* multiple excitations within the active MO space

*Huge calculations, limited to small systems (<20 atoms)*

**Accuracy**: HF < IC < CAS-SCF

*for a given basis set and a given active MO space*
APPLICATION TO ABSORPTION SPECTROSCOPY

Accessible quantities from CI calculations

Transition energies and wavelengths

ΔE, \( \lambda \)

Transition dipoles

\[ \bar{\mu}_{0e} = -e \langle \Psi_0 | \vec{r} | \Psi_e \rangle \]

Unit = C.m
1 a.u. of \( \mu = 8.478358 \times 10^{-30} \) C.m = 2.5415 D

Oscillator strengths

\[ f_{0e} = \frac{2}{3} \frac{\Delta E}{|\bar{\mu}_{0e}|^2} \]

Dimensionless (proportional to the absorption intensity)

Extinction coefficient \( \varepsilon \)

\[ f_{0e} \propto \int \varepsilon d\nu \]

With \( \varepsilon \) in mol\(^{-1}\).cm\(^{-1}\).L and \( \nu \) in cm\(^{-1}\), \( f_{0e} \approx 4.3 \times 10^{-9} \int \varepsilon d\nu \)
A CASE STUDY: THE ETHYLENE MOLECULE

Ethylene molecule
SCF/AM1 calculation

FINAL HEAT OF FORMATION = 16.471116 kcal
= 68.931621 kJ

ELECTRONIC ENERGY = -737.526966 eV

CORE-CORE REPULSION = 427.165969 eV

TOTAL ENERGY = -310.360997 eV

GRADIENT NORM = 0.004842

RMS GRADIENT NORM = 0.001398

IONIZATION POTENTIAL = 10.551419 eV

HOMO–LUMO GAP = 11.989210 eV

Alpha MOs

4 Frozen Core Electrons
Ethylene molecule
Cl(6,7)/AM1 calculation (frozen geometry)

Start from the geometry optimized at the SCF/AM1 level
Job type = Energy

Number max. of Slater determinants used to build the CI matrix

Active space definition

Number of states to be printed in the .out file

Reference state (the state under study)

Print options
Ethylene molecule
Cl(6,7)/AM1 calculation (frozen geometry)

M.O. NUMBER :  6 7

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<th>CONFIGURATIONS CONSIDERED IN C.I.</th>
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RHF state \( \Phi_1 \)

Single excitations \( \Phi_2 \) and \( \Phi_3 \)

Double excitation \( \Phi_4 \)

C.I. MATRIX (eV)

<table>
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**Ethylene molecule**  
CI(6,7)/AM1 calculation (frozen geometry)

### C.I. MATRIX (eV)

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**diagonalisation**

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<td>( 0.0000)</td>
<td>( 0.1889)</td>
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<td>( 0.0000)</td>
<td>( 0.0000)</td>
<td>( 0.9820)</td>
<td></td>
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</table>

**Cl ground state:**
\[ \Psi_1 = 0.9820\Phi_1 - 0.1889\Phi_4 \]

**First excited state (triplet):**
\[ \Psi_1 = 0.707\Phi_2 + 0.707\Phi_3 \]

**Second excited (singlet):**
\[ \Psi_1 = 0.707\Phi_2 - 0.707\Phi_3 \]
Ethylene molecule  
Cl(6,7)/AM1 calculation (frozen geometry)  

<table>
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</table>

Absorption spectrum  
$\lambda_{\text{max}} = 185.4 \text{ nm}$  

Transition dipole:  
$\vec{\mu}_{0e} = -e \langle \Psi_0 | \vec{r} | \Psi_e \rangle$  
Unit = C.m  
1 a.u. of $\mu = 8.478358 \times 10^{-30}$ C.m  
= 2.5415 D  

Oscillator strength:  
$f_{0e} = \frac{2}{3} \Delta E |\vec{\mu}_{0e}|^2$  
Dimensionless  
Proportional to the absorption intensity  

Extinction coefficient $\varepsilon$  
$f_{0e} \propto \int \varepsilon d\nu$ ; with $\varepsilon$ in mol$^{-1}$cm$^{-1}$L and $\nu$ in cm$^{-1}$, $f_{0e} \approx 4.3 \times 10^{-9} \int \varepsilon d\nu$
Ethylene molecule in its ground state
Cl(6,7)/AM1 calculation (HF geometry)

Electronic structure of the ground state: unchanged from SCF/AM1 (symmetry reasons)

Cl(6,7)/AM1 calculation (relaxed geometry)

Change in the geometry: $d_{C=C}$ increases by 0.015 Å due to the contribution of the double excitation in the ground state WF
APPLICATION TO EMISSION SPECTROSCOPY

Ethylene molecule
Cl(6,7)/AM1 calculation (geometry optimization of the first singlet excited state)

Keywords:
AM1 C.I.(6,7) CIDIP ROOT=2 SINGLET CISTATE=10 TRUSTE T=AUTO DEBUG MATCI MECI
or:
AM1 C.I.(6,7) CIDIP ROOT=3 CISTATE=10 TRUSTE T=AUTO DEBUG MATCI MECI

Compared to the ground state, $d_{C-C}$ increases by 0.076 Å
Intermediate between single and double bond
Ethylene molecule
Cl(6,7)/AM1 calculation (geometry optimization of the first singlet excited state)

<table>
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Emission spectrum

\[ \lambda_{\text{max}} = 198.8 \text{ nm} \]